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Short communication

# Enhancing the performance of a diazonium-modified carbon supercapacitor by controlling the grafting process

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ABSTRACT

The activated Norit carbon was modified by grafting the 4-nitrobenzenediazonium salt in the presence or in the absence of a radical scavenger (DPPH: 2,2-diphenyl-1-picrylhydrazyl) to produce modified carbon powders having different surface organic layers going from monolayer to multilayer. The surface chemistry and pore texture of carbon products were studied by TGA, chemical elemental analysis and nitrogen gas adsorption measurements. The resulting powders were used as active components in supercapacitors working in alkaline media to investigate the impact of the grafting on the electrochemical performances. Cyclic voltammetry and electrochemical impedance spectroscopy were used to investigate the charge/discharge process in aqueous 1 M KOH. The present work demonstrates that the high double-layer capacitance and the low ionic resistance of the pristine carbon can be preserved by limiting the growth of the grafted layer with DPPH.

## 1. Introduction

Activated carbons are attractive materials for electrochemical charge storage applications, due to their high specific surface area and their facile surface chemical functionalization, which allows the preparation of heteroatom-enriched porous carbons [1] and molecule–carbon composites [2] prior to their implementation into storage devices at the frontier between electrochemical capacitors and batteries [3]. Despite promising results, recent studies show that the improved capacitance obtained by chemical treatments of carbon is often achieved at the expense of the double-layer capacitance, especially when redox molecules are grafted on the carbon surface [4]. Indeed, activated carbons in such hybrid materials do not maintain their high double-layer capacitance and their low ionic resistance, due to a dramatic decrease in the surface BET caused by the accumulation of molecules at the entrance of micropores [5–7].

In order to derive the maximum benefit from the redox groups introduced, solutions must be found for minimizing the impact of the chemical treatment on the efficiency of the electrochemical charge storage at the carbon/electrolyte interface. In a very recent work, T. Breton et al. present a simple strategy to avoid the formation of multilayer films during the chemical derivatization of carbon surface by diazonium chemistry [8,9]. Their approach consists to use a radical scavenger in solution to limit the growth of the surface layer by short-circuiting the radical propagation reaction occurring by the attack of reactive aryl radicals on molecules already attached to the surface. By using this strategy, the control of the layer growth is assumed to be dependent to the electronic properties of the para substituent of the diazonium salt, and it seems that withdrawing substituents are requisite for obtaining a monolayer [10]. So, in the present work, the well-known 4-nitrobenzenediazonium salt (NBD) is used, in combination with 2,2-diphenyl-1-picrylhydrazyl (DPPH) as radical scavenger, to ensure that a better control of the grafting step is an efficient means to curb the negative impact of the grafting on the intrinsic properties of porous carbons. In this purpose, a nitrobenzene-modified carbon is prepared by spontaneous reaction of NBD on the activated Norit carbon in the presence or in the absence of DPPH. The impact of a radical scavenger on the grafting was investigated by thermal gravimetric analysis (TGA), elemental chemical analysis and nitrogen gas adsorption measurements. The attached nitrobenzene groups are further easily converted into hydroxylamine/nitroso groups, acting as two-electron surface redox groups for improve the specific capacitance in aqueous supercapacitors. Cyclic voltammetry and electrochemical impedance spectroscopy (EIS) serve to determine to which extent the double layer capacitance and the ionic transport within the porous structure of carbon can be preserved by limiting the growth of the grafted layer with a radical scavenger.

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## 2. Experimental section

### 2.1. Reagents

Carbon powder (Norit-S50) was obtained from Norit, 4-nitrobenzenediazonium salt (97%), and 2,2-diphenyl-1-picrylhydrazyl were purchased from Aldrich. Norit carbon is a microporous activated carbon having a specific BET surface area of 1231 $m^2\ g^{-1}$, an average pore diameter of 12 Å and a total pore volume of 0.647 $cm^3\ g^{-1}$.

### 2.2. Material preparation and characterization

For the modification of the carbon powder with redox molecules, 200 mg of carbon Norit-S50 (NS) was dispersed in 50 mL of acetonitrile (HPLC grade) by sonication for 30 min and then 190 mg of 4-nitrobenzenediazonium salt (0.05 eq. versus carbon) was added with and without 630 mg of 2.2-diphenyl-1-picrylhydrazil (0.1 eq. versus carbon). After stirring at room temperature for 24 h, the reaction mixture was vacuum filtered on a Teflon filtration membrane (from Sartorius Stedim) having a pore size diameter of 0.2 μm. After reaction, the modified carbon powder was thoroughly washed successively with acetonitrile (100 mL), DMF (100 mL), methanol (100 mL) and acetone (100 mL). The nitrobenzene-modified carbon powders were dried overnight at 80 °C.

TGA analyses of carbon products were performed with a Netzch STA449 F3 apparatus with 15 mg typical mass of materials. Chemical compositions of carbon powders were determined with an organic elemental analyzer from Thermo (model FLASH 2000). The porous texture of carbons was analysed by adsorption–desorption measurements using nitrogen as adsorbent at 77 K with a micromeritics ASAP 2010 apparatus. The pore size distribution was obtained by treatment of the isotherms by DFT Monte-Carlo calculations.

### 2.3. Electrode preparation and electrochemical measurements

Electrodes were prepared by mixing the activated carbon powder with polytetrafluoroethylene (PTFE, 60 wt% dispersion in water) used as binder and carbon black (superior graphite) with a ratio of 75:10:15 (wt;wt;wt) in a small volume of ethanol until a homogeneous carbon paste was obtained. The carbon paste was spread to obtain a thin film which was dried at 80 °C for 1 h. A sample of some milligrams was pressed for 60 s at 1 MPa between two stainless steel grids (80 mesh, 0.127 mm, Alfa Aesar) used as current collector.

Electrochemical measurements were achieved at room temperature in 1 M KOH with a three-electrode cell composed of a working electrode in conjunction with a Norit electrode as counter electrode and an Ag/AgCl system as reference electrode. A potentiostat|galvanostat model VSP (from Bio-Logic) monitored by ECLab software was used. For the EIS study, the measurements were conducted at $-0.1$ V with an ac potential amplitude of 5 mV and a frequency range of 100 kHz–10 mHz.

## 3. Results and discussion

The grafting conditions and the chemical properties of the grafted layer are given in Table 1, which reveals that different molecule loadings are produced in the presence or in the absence of DPPH. Bulk-sensitive techniques such as TGA and chemical elemental analysis, demonstrate that the grafting yield in the presence of DPPH is only half the one in the absence of DPPH, in good agreement with a recent study showing that the formation of multilayers from diazonium salts can be limited by the DPPH radical scavenging activity (a part of the active aryl radical species produced by homolytic dediazotization is captured by DPPH) [10]. When the phenyl ring is strongly deactivated by an electron-withdrawing substituent, the first grafted molecules directly linked to the surface show a lower reactivity towards electrophilic attack, forming a monolayer.

In order to investigate the impact of the grafting on the textural properties of the porous carbon in the presence or in the absence of DPPH, Fig. 1 shows the pore size distribution, as well as the cumulated surface in inset, deduced to the adsorption–desorption isotherms of nitrogen at 77 K for unmodified Norit carbon and carbon modified with and without DPPH. The pristine Norit carbon presents micropores with diameter between 10 and 20 Å and small mesopores between 20 and 40 Å. Following the attachment of nitrobenzene molecules without DPPH, an important loss of the microporous and mesoporous surface is observed. The BET specific surface area is drastically reduced, changing from 1231 to 506 $m^2\ g^{-1}$, and the total pore volume decreases from 0.647 to 0.249 $cm^3\ g^{-1}$. On the contrary, when DPPH is used, the modification has a smaller impact on the porous structure of the carbon. After grafting in the presence of DPPH, $S_{BET} = 980\ m^2\ g^{-1}$ and the pore volume is found to be 0.516 $cm^3\ g^{-1}$. This is clearly evidenced by the cumulated surface area shown in the inset of Fig. 1, which reveals that the micropore surface area, suitable for enhancing capacitance, remains virtually unchanged.

The effective control of the grafting process by the scavenging activity of DPPH is expected to have a direct impact on the electrochemical performance of the molecule–carbon composite material. Fig. 2A compares the cyclic voltammograms (CVs) in 1 M KOH at 5 $mV\ s^{-1}$ of unmodified carbon electrode and carbon electrodes modified in the presence and in the absence of DPPH. Compared to the nearly pure capacitive CV of the unmodified carbon electrode, an electrochemically reversible system is obtained with molecule–carbon composites after complete conversion of nitro groups into the hydroxylamine groups by cycling the potential from 0 to $-1.2$ V at 5 $mV\ s^{-1}$ in the same alkaline electrolyte. This faradaic envelope corresponds to the two-electron surface redox activity of hydroxylamine/nitroso groups, which increase the specific capacitance from 60 to 129 ± 10.7 $F\ g^{-1}$ or 108 ± 11.6 $F\ g^{-1}$ (the standard error corresponds to the standard deviation of the repeatability calculated from 3 measurements), as the grafting occurred in the absence or in the presence of DPPH. Note that the increase in specific capacitance is nearly the same with or without DPPH, whereas the molecule loading varies by twice. This agrees well with previous studies showing that the nitro-containing surface layer becomes partially non-electroactive when the film becomes thicker [10]. The reason is a less electrolyte-accessibility of the inner redox groups located within the film, compared to that of the outer redox groups present at the solid/liquid interface [11]. So, the use of DPPH during the grafting process allows increasing the overall capacitance while minimizing the loading of inactive components in the electrode, which results in an increase in the energy density. Furthermore, noticeable changes in the CV profiles are obtained according to whether DPPH is

**Table 1**
Grafting conditions and chemical properties of carbons.

| Carbons | Grafting conditions | | Elemental analysis [a] | | TGA<br>Mass loss at 800 °C under Ar (wt%) |
|---|---|---|---|---|---|
| | Eq. NBD | Eq. DPPH | wt% N | wt% O | |
| NS | – | – | 0 ± 0.01 | 1.48 ± 0.14 | – |
| NS without DPPH | 0.05 | – | 3.75 ± 0.03 | 6.60 ± 0.02 | 11 |
| NS with DPPH | 0.05 | 0.1 | 1.42 ± 0.02 | 3.90 ± 0.04 | 6 |

[a] The standard error corresponds to the standard deviation of the repeatability calculated from 3 measurements.